# INVESTIGATIONS

ON SOME

# NEW DERIVATIVES OF NAPHTHALENE.

---

INAUGURAL DISSERTATION

FOR THE ATTAINMENT

OF THE

DEGREE OF DOCTOR OF NATURAL SCIENCES

AT THE

UNIVERSITY OF TÜBINGEN,

UNDER THE PRESIDENCY

OF

**DR. RUDOLPH FITTIG,**

PROFESSOR IN ORDINARY OF CHEMISTRY,

PRESENTED

BY

J. P. BATTERSHALL

OF NEW YORK CITY.

---

TÜBINGEN, 1872.

PRINTED BY L. FR. FUES.

To a highly distinguished scientific faculty, I have the honor of presenting the following investigations as an Inaugural Dissertation for the degree of Doctor of Natural Sciences. In so doing, I take great pleasure in expressing my cordial thanks to Professor Fittig, who suggested their undertaking, and conducted their execution, for the uniform kindness and care which he has evinced toward me during my course at the Universities of Göttingen and Tübingen.

---

During the past twenty years, the science of chemistry has undergone what may well be termed a revolution. A wonderful accession of facts has been made, and new and important theories have been brought forward, and firmly established. It is only proper and necessary that all innovations should undergo a severe and thorough test. False ideas and problematical theories are only too often advanced, and were it not for that great test, experiment, the science of chemistry would be burdened with doubtful hypotheses, instead of being enriched with theories well proven and substantiated. In view of these facts, it is evident that the importance of the investigations made during this great epoch of chemical history cannot be overrated. Every additional link to the chain of our chemical knoweldge possesses at all times a high scientific value, and this is doubly true at a period when a reformed notation is being established, and when the identity and analogy of chemical compounds, previously unsuspected, is becoming clearly proven.

---

In considering the remarkable advance that organic chemistry has made within the last quarter of a century, one can hardly fail to notice, that no class of com-

pounds has enjoyed so large a share of attention, as the aromatic series. That this second great division of organic bodies should be especially favored, appears but natural when we remember the complex and important nature of these compounds. While benzol and its derivatives have busied the investigating chemist to a great extent, the homologous body naphthalene, has been comparatively neglected, and it appears especially desirable that our knowledge concerning the composition and characteristic properties of this body, and its derivatives, should be augmented by additional research. Naphthalene may be regarded as the prototype of a third grand division of organic compounds; marsh gas, and benzol being respectively, the analogous standards of the first and second series. Within the past few years, many contributions to the chemistry of naphthalene have been made. A series of acids has been discovered, and compounds possessing in every way the character of phenoles (naphtoles) and quinones, have been obtained. The compounds of naphthalene corresponding to methyl and ethyl-benzol, have also been prepared. All of these compounds exhibit the greatest similarity to the analogous compounds of the benzol series, and fully justify us in promoting naphthalene to the position of a typical body. The near relation in which naphthalene stands to benzol has lately been clearly proven by the classical investigations of GRÆBE [1]).

It was deemed of interest to see whether it was possible to obtain the aldehyde of the naphthalene

1) Deut. chem. Ges.-Ber. I, 36.

group, corresponding to the benzoic-aldehyd (oil of bitter-almonds).

Reasoning from analogy, it was expected, that by the action of hydrogen (in statu nascendi) on this aldehyde, an alcohol of the naphthalene series, corresponding to benzyl-alcohol, would be obtained. The following account of my investigations will show to what extent these expectations were fulfilled. In addition to the investigation of the naphthoic aldehydes, and their derivatives; researches were made on the action of sulphuric acid upon the α and β naphthoic acids. By fusing the potassium salts of the sulpho-acids thus formed, with potassic-hydrate, the formation of isomeric oxy-naphthoic acids was awaited. The question as to the identity, or isomerism of these acids with the two oxy-naphthoic acids already obtained by SCHÆFFER [1]), by the action of carbonic acid and sodium on α and β naphtholes, was sufficiently interesting, to induce an investigation in this direction.

---

Of the various methods for obtaining aldehydes usually employed, the one of distilling an intimate mixture of calcic-formiate and the calcium salt of the respective acid, appeared in this case the most practicable. An account of the method used to prepare the calcium salts of the two naphthoic acids may be of interest. In order to obtain the α and β monosulpho-acids of naphthalene, three parts of concentrated sulphuric acid, and four parts of naphthalene, were heated to a temperature of

1) Annalen der Chemie und Pharm. B. 152. S. 291.

90°. for ten to thirteen hours, the mixture being frequently shaken. The method used to prepare the acids, is essentially the same as that recommended by MERZ [1]). „The sulpho-acids formed are dissolved, by pouring the still warm mixture into about eleven times the amount of water. This mixture is heated to boiling, and an excess of plumbic-carbonate added to the solution, small quantities at a time. After the precipitate of plumbic-sulphate has settled, the clear solution is drawn off by means of a syphon. It is advisable to wash the precipitate of plumbic-carbonate with hot water, as a second dilute solution of the salts can be obtained by this means. The solution gives, when cold, a large amount of kernels or scales of the β lead salt. If any α lead salt is mixed with the β compound, it can be extracted by means of hot alcohol. The mother-liquor of the β salt contains the α compound. This is concentrated and allowed to cool, when the α salt falls down. The α lead salt resembles the corresponding β compound somewhat in appearance, but is soluble in water and alcohol to a far greater extent. By means of repeated concentration of the mother-liquor, the entire amount of the α salt can be obtained. The β salt is purified by means of crystallisation, the α salt by dissolving in alcohol, distilling the solution to dryness, and dissolving the residue in hot water. The solution is well shaken and after cooling gives the α salt, as a flake-like precipitate.“ According to MERZ [2]) it is easy to obtain at pleasure the α or β salts of the monosulpho-acids of naph-

1) Zeitschrift für Chemie. N. F. IV. 393.
2) Zeitschrift für Chemie. N. F. VI. 119.

thalene, by regulating the temperature to which the mixture of naphthalene and sulphuric acid is heated. The potassium salts of the α and β sulpho-acids are easily prepared from the lead salts, by the addition of potassic-sulphate, or carbonate, and filtering the hot solution. The β potassium salt resembles the corresponding lead compound, in being less soluble than the α salt. In order to prepare naphthalene-cyanide, the following method recommended by MERZ and MÜHLHAUSER [1]), was resorted to: an intimate mixture of potassic-cyanide and the α potassium salt of the monosulpho acid was prepared both compounds having been well dried. This mixture was heated to about 300°; at which temperature the α naphthalene readily distills over. The compound so prepared always contains small quantities of ammonic-cyanide and carbonate, which compounds however, do not exert an injurious influence, when the preparation of naphthoic acid is intended. By treating the β salt in the same manner, the β naphthalene-cyanide is obtained. The α cyanide remains fluid for several days; the corresponding β compound usually solidifies in a short time. Large quantities of the above mentioned mixture should not be taken at a time; the uniformity of temperature desirable being obtained, only when small amounts are used. By treating the α and β naphthalene-cyanides with an alcoholic solution of potassic-hydrate, the respective modifications of naphthoic acid are obtained [2]). The reaction is finished, as soon as

1) Zeitschrift für Chemie. N. F. VI. 397 und V. 70.

2) MERZ, Zeitschrift für Chemie. II. Jahrgang. 33.

the evolution of ammonia ceases. The operation in this instance was conducted in a glass flask, connected with an inverted LIEBIG'S condensor. Traces of ammonia were still given off after three days heating. According to MERZ, a complete reaction takes place in two or three hours, when a closed iron digestor is used. When the operation is finished, the alcohol is distilled off, and the remaining potassic-naphthoate dissolved in hot water. This alkaline compound is decomposed by the addition of hydrochloric acid, the naphthoic acids falling down, as a white bulky precipitate. On one occasion, as the formation of β naphthoic acid was especially desired, naphthalene was heated to 200°, with somewhat more sulphuric acid than is necessary to produce the α and β monosulpho-acids of naphthalene. Under these circumstances no α acid was obtained. The greater portion of naphthoic acid prepared from the naphthalene-cyanide was of the β modification. Together with this, quite a large quantity of dicarbo-naphthoic acid [1]) was produced. This fused at a temperature higher than 290°., and is evidently identical with the acid obtained by DARMSTÆDTER and WICHELHAUS, from naphthalene-dicyanide [2]). Its further investigation was therefore not undertaken. It is of interest to note, that α naphthoic acid has been obtained by several other methods. HOFMANN at first obtained the amide of the acid, by distilling naphthyl-amine with oxalic acid, and treating the nitrile

---

1) $= C^{10} H^6 \begin{matrix} CO.OH. \\ CO.OH. \end{matrix}$

2) Annalen der Chemie und Pharm. B. 152. 309.

compound so formed with caustic alkali [1]). EGHIS prepared the acid, by treating brominated naphthalene with chlor-carbonic ether, in presence of sodium amalgam [2]); and MEYER finally melted the α potassium salt of the monosulpho-acid with sodic-formiate, and obtained the α naphthoic acid [3]). In order to obtain the calcium salts, hot aqueous solutions of the acids were neutralised with finely pulverized calcic-carbonate, or calcic hydrate, the fluid filtered, and the salts allowed to crystallise.

---

1) Annalen der Chemie und Pharm. B. 142. 127.
2) Ibid. B. 154. 250.
3) Ibid. B. 156. 274.

# I.

## Naphthoic aldehyde.

The $\alpha$ calcium salt obtained in this manner, was intimately mixed with calcic-formiate, and strongly heated in a glass retort. It first the mass melted, and copious fumes were given off. As soon as the evolution of fumes had discontinued, a dark colored oil distilled over. This was separated from the naphthalene present, by means of a concentrated solution of hydric-sodic sulphite, the insoluble compound common to aldehydes being formed. This gave when decomposed with sodic-carbonate, the oil in a pure state [1]). Several combustions gave results that agreed exactly with the formula: $C^{11} H^8 O$ ($= C^{10} H^7 - CHO$), and the oil was supposed to be the pure naphthoic aldehyde. It was later observed, however, that by long standing, crystals were formed in the oil, and the suspicion was aoused that the substance under investigation was a mixture. In order to decide this question conclusively, the oil was oxidized with potassic-permanganate. It was found that the naphthoic acid formed, did not fuse at a constant temperature, — in other words, was not pure. As the impurity could only originate from the incomplete

---

1) The oil so obtained is somewhat heavier than water, possesses a burning, aromatic taste, and boils at 280°.

separation of the isomeric naphthoic acids, these were again prepared, and subjected to a second separation, by means of the different solubility of the calcium salts [1]). The acids thus prepared were absolutely pure, and possessed respectively the fusing points, 160°, and 182°. The pure calcium salt of the α naphthoic acid was treated as described above with calcic-formiate. To my astonishment no aldehyde, or at least, only a trace was formed, almost the entire amount of the salt being decomposed into naphthalene and calcic-carbonate. This agrees with the results of HOFMANN, who also failed to obtain the aldehyde of α naphthoic acid in a pure state [2]). The temperature at which the α calcium salt is decomposed into naphthalene and calcic-carbonate, is evidently lower, than the temperature, at which the mixture of the salts react on each other. I repeated the operation three times, but only obtained negative results. The investigations of MERZ and WEITH [3]), indicate, that the α monosulpho-acid is much more unstable than the corresponding β compound. The *alpha* class of compounds of the naphthalene series appears generally, to be more easily decomposible, than the isomeric *beta* modification. It is remarkable that when the α calcic-naphthoate is mixed with a comparatively small amount of the iso-(β) acid salt, as was the case in my first experiments, it apparently joins in the reaction; as the fluid aldehyde,

---

1) The α salt is soluble in 93 parts of water at 15°. — The β salt in 1,400 — 1,800 parts at the same temperature.

2) Deut. chem. Ges. Ber. I. 43.

3) Ibid. III. 195.

which was at first obtained, possessed entirely different properties from the aldehyde of iso-naphthoic acid.

## II.

### Isonaphthoic aldehyde.

An intimate mixture of equal parts of calcic-isonaphthoate and calcic-formiate was subjected to a strong heat in a glass retort, both salts having been dried. The reaction took place in the same manner as with the α calcium salt, with the exception, that only a very small amount of naphthalene was produced. The compound with hydric-sodic-sulphite was separated from the remaining fluid by filtration, and well dried, by pressing between filter paper [1]). Any naphthalene that was still present, was got rid of, by washing the compound repeatedly with ether. The compound thus purified, is perfectly white, and is insoluble in water and ether. It is easily decomposed by sodic-carbonate, the iso-aldehyde being set free. It was found to be convenient to distil the mixture of the hydric-sodic-sulphite compound, and sodic-carbonate, water being added. The iso-aldehyde distills over readily with water vapour. A little ether was added to the mixture of aldehyde and water, and the fluid well shaken. The solution in ether thus obtained, was drawn of with a pipette, and the ether removed by distillation. The reaction in the formation of the iso-aldehyde is:

---

1) This compound probably has the formula:

$$C^{10}H^{7} - CH \begin{cases} OH \\ SO^{3}\,Na. \end{cases}$$

$(CHO^2)^2Ca + (C^{11}H^8O^2)^2Ca = 2(C^{11}H^8O) + 2(CaCO^3)$

The iso-naphthoic-aldehyde is a white crystalline body, easily soluble in alcohol and ether. In cold water it is insoluble, in boiling water somewhat. From an aqueous solution it separates in voluminous, thin, shining plates. It was obtained in the same form, by evaporation of the alcoholic solution. The iso-aldehyde fuses, instantaneosly and undecomposed, at the constant temperature of 59°.5. It possesses a weak aromatic odor, and is inflammable, burning with a bright, yellow flame. It was dried over sulphuric acid for several days, and analysed.

Combustion.

I. .1462 gr. substance gave .4565 gr. $CO^2$ = .1245 C = 85.15 pr. ct. and .0775 gr. $H^2O$ = .0086 H = 5.88 pr. ct.

II. .2312 gr. substance gave .7159 gr. $CO^2$ = .1952 C = 84.42 pr. ct., and .1059 gr. $H^2O$ = .0117 H = 5.07 pr. ct.

| Calculated | Found | |
|---|---|---|
| | I. | II. |
| C 84.61 | 85.15 | 84.42 |
| H 5.12 | 5.88 | 5.07 |
| O 10.27 | | |
| 100.00 | | |

When heated with potassic-permanganate, the iso-naphthoic aldehyde is readily oxidized to iso-naphthoic acid, manganic hydrate separating. Repeated attempts were made to convert the aldehyde $C^{10}H^7 - CHO$ into the corresponding alcohol, $C^{10}H^7 - CH^2.OH$ by means of

sodium amalgam. The iso-aldehyde was heated in a flask, connected with an inverted LIEBIG'S condensor, with sodium amalgam for several hours. As alkaline solutions often react upon aldehydes, some sulphuric acid was added to neutralize the sodic solution formed by the decomposition of the amalgam. Although the reaction was attempted in several other ways, the results obtained were negative. The substance formed was uncrystalline, and difficult to purify, and it was considered impracticable to investigate it further. The iso-aldehyde is easily dissolved by warm concentrated nitric acid. The product formed, reacts neutrally and is separated from its acid solution, upon addition of water. It was found however to be impossible to obtain a sufficient quantity of this nitro-compound, for investigation.

## III.

### Action of an alcoholic solution of ammonia on iso-naphthoic aldehyde.

The iso-naphthoic aldehyde is easily soluble in a concentrated alcoholic solution of ammonia. The solution is allowed to stand for several days, the aldehyde separating as an insoluble amido-compound, on the sides and bottom of the vessel in which the solution is contained. This was separated from the mother-liquor, dried in the air, and analysed.

Combustion.

.1311 gr. substance gave .4249 gr. $CO^2$ =
.1158 C = 88.32 pr. ct. and .0666 gr. $H^2O$ =
.0074 H = 5.64 pr. ct.

The nitrogen determination was made, by decomposing the compound with hydrochloric acid, and estimating the amount of platinum contained in the ammonio-platinic-chloride

.0515 gr. substance gave .0635 gr. Pt.
= .0090 gr. N = 5.94 pr. ct.

| Calculated for $C^{33} H^{24} N^2$. | | Found. |
|---|---|---|
| C | 88.39 | 88.32 |
| H | 5.35 | 5.64 |
| N | 6.26 | 5.94 |
| | 100.00 | 99.90 |

By allowing the mother-liquor to stand for a day or two, a further formation of this amido-compound takes place. In this manner the entire ammount of the compound can be obtained. This compound is, without doubt, analogous to hydrobenzamide, $(C^6 H^5 - C H)^3 N^2$, and has the constitution $(C^{10} H^7 - C H)^3 N^2$.

As a proper name I propose hydroisonaphthamide. The reaction in the formation of this substance is

$$3\,(C^{10}H^7 - CHO + 2\,(NH^3) = (C^{10}H^7.CH)^3N^2 + 3\,H^2O.$$

The hydroisonaphthamide forms hard, colorless, warty crystalls. These consist of alternately light and dark colored concentric rings. It is insoluble in water, and cold ether and alcohol. By boiling with water, it is not decomposed. In this it differs essentially from the corresponding hydrobenzamide, which when boiled with water, is decomposed into the oil of bitter-almonds, and ammonia. When treated with a dilute solution of hydrochloric acid, and slightly warmed, the hydroisonaphthamide is easily, and completely, decomposed into

isoaldehyde, and ammonic-chloride, according to the reaction:

$$(C^{10}H^{7} - CH)^{3}N^{2} + 2\,HCl + 3\,H^{2}O = 3\,(C^{10}H^{7} - CHO) + 2\,NH^{4}\,Cl.$$

It was by means of this reaction, that the nitrogen estimation was made in the above analysis. By heating with alcohol or ether, the hydroisonaphthamide suffers an analogous decomposition, the isoaldehyde being formed in both cases. The hydroisonaphthamide fuses at 146°—150°; at this temperature, however, it undergoes an alteration, and is changed into a yellow, glass-like, solid substance.

## IV.

### Action of fuming sulphuric acid on naphthoic acid.

Naphthoic acid, pure and well dried, was treated for 24 hours with cold, fuming sulphuric acid. The acid was dissolved in large quantities, to a thick, dark-colored fluid. This was poured into about twelve times the amount of warm water; no naphthoic acid being separated by this treatment. Two sulpho acids were contained in this solution. I will designate these as *alpha* and *beta* Sulphonaphthoic acids. The salts of the α sulpho-acid are much less soluble in water, and show far greater tendency to crystallize, than the isomeric β salts. The aqueous solution of the two acids was heated to boiling, and neutralized with baric-carbonate. After filtering from the baric-sulphate, the solution of the α and β barium salts was evaporated to a small volume. The crystals that at first separated out, were nearly pure α sulpho-naphthoate, the greater portion of the β salt remaining in the mother-

liquor. By means of repeated recrystallisation, a complete separation of the two salts was effected.

α *Sulpho-naphthoic acid.* $C^{10}H^6 < \begin{matrix} CO.OH \\ SO^2.OH \end{matrix}$

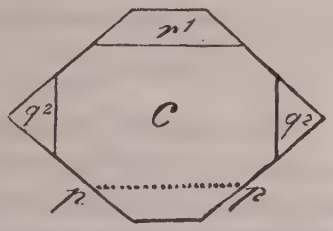
The free acid was obtained from a solution of the α baric-sulpho-naphthoate, by exact precipitation with sulphuric acid. After filtering from the baric-sulphate precipitate, the acid solution was evaporated over a water bath, nearly to dryness, and placed over sulphuric acid.

In this way the acid was obtained in thin, colorless needles. These are very soluble in water, but are not deliquescent. The acid fuses at 230°—240°. At this temperature it appears to undergo a slight decomposition. The following salts were prepared, and investigated:

α *Baric-sulpho-naphthoate.* $C^{10}H^6 < \begin{matrix} CO.O \\ SO^2.O \end{matrix} > Ba + 4H^2O.$

This salt was obtained by neutralizing a solution of the α sulpho-acid, with baric-carbonate. It crystallizes, from an aqueous solution, in large, transparent crystals. These are with difficulty soluble in water. Owing to the kindness of Professor von REUSCH; I am enabled to subjoin a more minute description of these crystals:

The crystals are monoclinic. The four reflecting faces *p*, with the oblique base *c* (which is always somewhat arched, and is bent toward the smaller diagonal of *c*), can he considered the main prism.



Two faces corresponding to $r'$ were noticed. These are parallel to the longer diagonal of $c$. The four side corners of the main prism are cut off by the small faces $q^2$ of a rhombic column. The axes of $q^2$ lie parallel to the small diagonal of $c$. In only a few crystals, all four faces exist. The obtuse angle of the main prism; which is halved by the median plane, $= 104^0.50'$. $cr' = 107^0 8'$, and $cp = 104^0 36'$. The acute angle of the rhombic prism $q^2 =$ extended over $c$, $42^0 50'$.

If $c = (001)$, $p = (110)$, and $r' = (\bar{1}01)$, the relations of the axes are:

$$a : b : c = 0.811 : 1 : 1.332.$$

The angle of the axes $a$ and $c$ in the median plane $= 108^0 29'$ and $q^2 = (021)$.

The salt was dried in the air, and the water of crystallisation estimated at $130^0$—$170^0$.

Analysis.

.3618 gr. salt gave .1825 gr. Ba $SO^4$
$=$ .10687 Ba $=$ 29.53 pr. ct., and
.055 gr. $H^2O = 15.20$ pr. ct.

| Calculated. | | Found. |
|---|---|---|
| Ba | 29.84 | 29.53 |
| $H^2O$ | 15.68 | 15.20 |

α *Calcic sulpho-naphthoate.*

$$C^{10}H^6 \begin{matrix} CO.O \\ SO^2.O \end{matrix} > Ca + 3\ H^2O.$$

Was prepared by neutralizing the solution of the α sulpho-acid, with calcic-carbonate. It crystallises from an aqueous solution in kernels, consisting of beautiful thin plates. These were dried in the air, and analysed.

Analysis.

I. .3045 gr. salt gave .117 gr. $CaSO^4$ = .0344 Ca = 11.29 pr. ct.

II. .2439 gr. salt gave .0926 gr. $CaSO^4$ = .02723 Ca = 11.16 pr. ct., and .0371 gr. $H^2O$ = 15.21 pr. ct.

| | Calculated. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Ca | 11.62 | 11.29 | 11.16 |
| $H^2O$ | 15.69 | | 15.21 |

The water of crystallisation was given off at 180°. at 150°. only $2^1/_2$ molecules $H^2O$ were driven off.

α *Potassic sulpho-naphthoate.* $C^{10}H^6 < \begin{matrix} CO.OK \\ SO^2.OK \end{matrix} + 2\,H^2O$.

This salt was obtained, by adding potassic-sulphate to a boiling solution of the α barium salt. It is much more soluble in water than the corresponding barium and calcium salts. Upon filtering from the precipitate of baric-sulphate, and evaporating the salt solution nearly to dryness, is was obtained in colorless thin plates. These were dried in the air, and analysed.

Analysis.

.2335 gr. salt gave .111 gr. $K^2SO^4$ = .0499 K = 21.37 pr. ct., and .0235 gr. $H^2O$ = 10.06 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| K | 21.47 | 21.37 |
| $H^2O$ | 9.88 | 10.06 |

The water of crystallisation was given off at 150°.

α *Cupric sulpho-naphthoate.*

$$C^{10}H^{6} < \begin{matrix} CO.O \\ SO^{2}.O \end{matrix} > Cu + 3\,H^{2}O.$$

This salt separates from a solution of the α potassium salt upon addition of cupric-sulphate, as a bluish-green precipitate. It is difficultly soluble in water, and crystallizes with 3 molecules of water. These are given off at 140°.

β *Baric sulpho-naphthoate.*

$$C^{10}H^{6} < \begin{matrix} CO.O \\ SO^{2}.O \end{matrix} > Ba + 4\,H^{2}O.$$

This salt was prepared, by neutralizing an aqueous solution of the β sulpho-acid, with baric-carbonate. It is very soluble in water, and shows little tendency to crystallize. The salt was dried in the air and analysed.

Analysis.

.3874 gr. salt gave .1969 gr. Ba $SO^{4}$ = .11577 Ba = 29.88 pr. ct., and .0582 gr. $H^{2}O$ = 15.02 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| Ba | 29.84 | 29.88 |
| $H^{2}O$ | 15.68 | 15.02 |

β *Calcic-sulpho-naphthoate.*

$$C^{10}H^{6} < \begin{matrix} CO.O \\ SO^{2}.O \end{matrix} > Ca + 1^{1}/_{2}\,H^{2}O.$$

This was obtained from the β barium salt, by exact precipitation with a solution of calcic-sulphate. The salt forms a fine crystalline powder. It was dried in the air and analysed.

Analysis.

.4971 salt gave .2091 gr. Ca $SO^4$ = .0615
Ca = 12.37 pr. ct., and .044 gr. $H^2O$ = 8.85 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| Ca | 12.61 | 12.37 |
| $H^2O$ | 8.51 | 8.85 |

The water of crystallisation was given off at 130°.

## V.

### Action of fused potassic-hydrate on α potassic sulpho-naphthoate.

α Potassic-sulpho-naphthoate, well dried, and pulverized, was added, in small portions at a time, to fused potassic hydrate. The mixture was heated in a silver crucible for about ten minutes, the mass being constantly stirred. The mass became yellow, and finally melted to a dark colored fluid. As soon small portion of this liquid gave no precipitate, when treated with water, the reaction is finished. Upon dissolving the cold alkaline salt in hot water, and decomposing it with hydrochloric acid, a white crystalline substance was precipitated, with evolution of sulphurous acid. This was filtered from the mother-liquor, purified by recrystallisation, from water, and dried for several days, over sulphuric acid. The analysis gave the following results:

I. .2381 gr. substance gave .6061 gr. $CO^2$ = .1653 C = 69.42 pr. ct., and .0956 gr. $H^2O$ = .01062 H = 4.46 pr. ct.

II. .1585 gr. substance gave .4067 gr. $CO^2$ = .1109 C = 69.96 pr. ct., and .0567 gr. $H^2O$ = .00639 H = 4.03 pr. ct.

III. .2248 gr. substance gave .087 gr. $H^2O$ = .00966 H = 4.29 pr. ct.

| Calculated. | | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| C | 70.21 | 69.42 | 69.96 | |
| H | 4.25 | 4.46 | 4.03 — | 4.29 |
| O | 25.54 | | | |
| | 100.00 | | | |

These figures correspond to the formula:

$$C^{11}H^8O^3 = C^{10}H^6 < \begin{matrix} OH \\ CO.OH. \end{matrix}$$

The reaction of formation of this oxyacid is:

$$C^{10}H^6 < \begin{matrix} CO.OK \\ SO^2.OK \end{matrix} + K(OH) = C^{10}H^6 < \begin{matrix} CO.OK \\ OH \end{matrix} + K^2SO^3.$$

Only a small amount of carbonic acid was evolved, upon decomposing the α potassic-oxynaphthoate with hydrochloric acid. The α oxynaphthoic acid is easily soluble in alcohol, and in an excess of boiling water. From an aqueous solution, it separates upon cooling, in beautiful thin feathery crystals. Attempts made to crystallize the acid from an alcoholic solution, were unsuccessful. By sublimation, the acid can be obtained in white feathery crystals. The α oxynaphthoic acid fuses at 234°—237° under slight decomposition. A dilute aqueous solution of the acid, gives, when treated with ferric-chloride, a dirty violet precipipitate.

The α baric-oxynaphthoate was prepared, by neu-

tralising a solution of the acid, with baric-carbonate. The salt is very easily soluble in water, and could not be obtained in well formed crystals. For this reason an analysis was deemed unnecessary.

## VI.

### Action of fused potassic hydrate on β potassic-sulphonaphthoate.

β Potassic-sulpho-naphthoate was fused with potassic-hydrate, in the same manber as the corresponding α salt. The reaction took place in the same manner. Upon separating, and investigating the acid formed, it was found to possess a fusing point ranging from 195° to 210°. Doubtless this behavior was due to the presence of some α oxyacid. Repeated attempts to obtain the pure acid by means of fractional crystallisation were unsuccessful, although the β oxyacid is somewhat more soluble in water, than the isomeric α acid. A separation of the two acids by means of the calcium salts, was found to be impracticable, as both salts are very easily soluble in water, and could not be obtained in well defined crystals.

## VII.

### Action of sulphuric acid on iso-naphthoic acid.

Perfectly dry iso-naphthoic acid was treated for 24 hours with fuming sulphuric acid. The acid is dissolved in a large amount, to a syrup-like fluid, which exhibits, in reflected light, a blue fluorescence. Upon pouring this

into warm water, neutralising the acid solution with baric-carbonate, and filtering from the insoluble baric-sulphate, a solution of the barium salts was obtained. It was found to be impossible, to separate the different isomeric salts from this solution, by fractional crystallisation, as they possessed nearly the same degree of solubility in solvents. It was therefore dertermined to convert the mixture of neutral salts into the corresponding acid salts. This was effected by dividing the solution into two equal parts, and precipitating the barium from one of these with exactly the required ammount of sulphuric-acid. This solution of the free sulpho-acids, was then added to the neutral salt solution, and the fluid concentrated somewhat by evaporation. Upon cooling, an acid salt separated, which was found to possess the properties of a pure compound. This salt was investigated. The other acid salt (or salts) could not be obtained, in crystalline form. Owing to this, as well as to scarcity of material, further investigations of these salts were not undertaken.

*Acid baric iso-sulphonaphthoate.*

$$C^{10}H^{6}\begin{cases}CO.\ OH\\ SO^{2}.\ O\end{cases}>Ba + 6\,1/2\,H^{2}O.$$
$$C^{10}H^{6}\begin{cases}CO.\ O\\ SO^{2}.\ OH\end{cases}$$

This salt was prepared as described above. It is nearly insoluble in cold water; pretty easily, however, in boiling. Upon cooling its aqueous solution, it crystallises in beautiful long plates. These were dried in the air, and analysed.

Analysis.

.339 gr. salt gave .0535 gr. $H^2O$ = 15.78 pr. ct., and .103 gr. Ba $SO^4$ = .06056 Ba = 17.86 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| Ba | 18.10 | 17.86 |
| $H^2O$ | 15.48 | 15.78 |

The water of crystallisation was given off at 140°.

*Baric iso-sulpho-naphthoate.* $C^{10}H^6 < \begin{matrix} CO.O \\ SO^2.O \end{matrix} > Ba + H^2O$.

This salt was obtained by neutralising a solution of the acid salt, described above, with baric-carbonate. It is very easily soluble in water. It crystallises brom a concentrated solution in well formed monoclinic, or triclinic crystals. The salt was dried in the air, and analysed.

Analysis.

.1365 gr. salt gave .0775 gr. Ba $SO^4$ = .4556 Ba = 33.37 pr. ct., and .007 gr. $H^2O$ = 5.12 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| Ba | 33.82 | 33.37 |
| $H^2O$ | 4.44 | 5.12 |

The water of crystallisation was driven off at 160°.

## VIII.

### Action of fused potassic-hydrate on acid potassic iso-sulphonaphthoate.

Acid potassic iso-sulphonaphthoate was fused with potassic-hydrate, in the same manner, as the salts already

described. The isoxy-acid formed, was separated by the same method as the other oxy-acids. The isoxynaphthoic acid resembles the isomeric α acid in appearance. It fuses instantaneously at 212°.—213°.; but becomes discolored at this temperature. The acid was dried at first, over sulphuric acid, then at 120°, at which temperature its weights remained constant, and analysed.

Combustion.

.1675 Gr. subsance gave .4209 gr. $CO^2$ = .1176 C = 70.20. pr. ct., and .069 gr. $H^2O$ = .00766 H = 4.57 pr. ct.

| | Calculated. | Found. |
|---|---|---|
| C | 70.21 | 70.20 |
| H | 4.25 | 4.57 |
| O | 25.54 | |
| | 100.00 | |

This result agrees with the formula:

$$C^{10}H^6 < \begin{matrix} OH \\ CO.OH \end{matrix}$$

The baric isoxynaphthoate is easily soluble in water. It separates, upon evavopation of the aqueous solution nearly to dryness, as a brown, resinous mass. Upon addition of alcohol to its watery solution, it is thrown down as a brown, bulky precipitate. Plumbic-isoxynaphthoate is obtained, as an insoluble precipitate, upon addition of plumbic-acetate to a solution of the isoxy-acid. A neutral, aqueous, solution of ammonic-isoxynaphthoate was treated with the following reagents:

$Ag\,NO^3$. Gave a white precipitate, which was reduced to metallic silver upon boiling the solution.

$Fe\,Cl^3$. Gave, at first, a light, yellow, turbidity, then then a reddish precipitate. Upon boiling the solution, the precipitate became black.

$Zn\,SO^4$. Gave no precipitate.

$Cu\,SO^4$. Gave a light grey precipitate, which remained unaltered upon boiling the solution.

As the cupric-isoxynaphthoate appeared to be stable, it was dried at $80^0$, and a copper estimation made.

Analysis.

.1313 gr. salt gave .0243 gr. Cu 0 = .0194 Cu
= 14.77 pr. ct.

| Calculated. | Found. |
|---|---|
| Cu 14.49 | 14.77 |

This result agrees with the formula:

$$C^{10}H^6 \begin{cases} OH \\ CO.O \end{cases} > Cu.$$
$$C^{10}H^6 \begin{cases} CO.O \\ OH \end{cases}$$

It is remarkable that most of the salts of the isoxynaphthoic acid are so unstable, as to suffer oxidation in aqueous solutions.

## IX.

### Concluding remarks.

The results of the foregoing investigations may be classified as follows:

1st. An aldehyde of naphthoic acid cannot be obtained in a pure state, by the distillation of a mixture of a

calcic-naphthoate, and calcic-formiate; or, at least, only traces of the pure aldehyde are produced by this reaction.

2nd. The isonaphthoic aldehyde can be be easily obtained in a pure condition, and possesses the characteristic properties of an aldehyde, in combining with hydric-sodic-sulphite, and forming a hydramido-compound, as well as in its general behavior. This is one of the few aldehydes that exist in a solid state [1]).

3rd. By the action of fuming sulphuric acid on naphthoic, and iso-naphthoic acids well characterized sulpho-acids are formed, a hydrogen atom being replaced by the monovalent group $SO^2.OH$. Two isomeric sulpho-acids were obtained from naphthoic acid. The isomeric relations of the iso-sulphonaphthoic acids were, however, not fully investigated.

4th. By fusing the potassium salts of α and β sulpho-naphthoic, and the acid potassium salt of iso-sulpho-naphthoic acid with potassic-hydrate, the hydroxyle group, OH, replaces the group $SO^2.OH$. None of the three oxyacids thus obtained, are identical with the oxynaphthoic acid obtained by SCHÆFFER [2]) by the action of carbonic acid and sodium upon α naphthole. This is proven by the reaction of these acids with ferric-chloride, as well as by the fusing points of the three acids [3]). It is impossible to say whether one

---

1) Palmitylic aldehyde ($C^{16}H^{32}O$) is also a solid.

2) Annalen der Chemie und Pharm. 152. 291.

3) The oxyacid prepared by SCHÆFFER from α naphthole, fuses at 186°—188°., and gives a pure blue coloration, upon addition of ferric-chloride.

of the oxy-acids obtained by me, is indentical with the acid obtained by SCHÆFFER from β naphthole, as the fusing point of this acid appears not to have been determined. The reaction of his β oxyacid with ferric-chloride, corresponds somewhat with the reaction of the oxyacids prepared by me.

Tübingen. August, 17th. 1872.